

Surface Modification of Nanoclays by Catalytically Active Transition Metal Ions

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A unique class of nanoclays was prepared by modification of pristine clays or organoclays (Cloisite C20A) with transition metal ions (TMIs). The composition, structure, morphology and thermal properties of TMI-modified nanoclays were investigated by atomic absorption spectroscopy (AAS), elemental analysis (EA), scanning electron microscopy (SEM), small-angle X-ray scattering (SAXS), wide-angle X-ray diffraction (WAXD), thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC) and X-ray absorption near-edge structure (XANES) spectroscopy. The content of TMIs in modified clays was found to be close to the limiting value of ion exchange capacity. SEM and X-ray results confirmed that TMIs were located between the mineral layers instead of being adsorbed on the surface of clay particles. TGA results indicated that the TMI treatment of organoclays could significantly increase the thermal stability, which was more pronounced in air than in nitrogen. Temperature-resolved SAXS measurements revealed that the presence of TMIs increased the onset temperature of structural degradation. The higher thermal stability of TMI-modified organoclays can be attributed to the change in the thermal degradation mechanism, resulting in a decrease in the yield of volatile products and the formation of char facilitated by the presence of catalytically active TMIs.

Introduction

The development of new polymeric materials with enhanced thermal stability and fire retardation property has been an active area of research to improve public safety. The common approach to prepare fire retardant (FR) polymers is not to make them noncombustible, but to render them less likely to ignite. If ignited FR-treated polymers would burn, they should burn less efficiently with self-extinguishing ability. Conventional FR additives such as halogenated organic compounds, organophosphorous compounds, aluminum, and magnesium hydroxides usually have an adverse effect on the mechanical properties of treated polymers. This is because these additives must be used at high loads in order to be effective, which can significantly degrade the mechanical properties. In addition, many of the conventional FR additives raise toxicity^{1–3} concerns. Thus, it is highly desirable to improve both flame retardation and mechanical properties simultaneously, that is, to design mechanical-reinforcing fillers that can also act as nontoxic FR agents.

The family of composites consisting of organically modified layered silicates (organoclays) and polymers may offer such an opportunity. Polymer–organoclay systems (so-called organoclay nanocomposites) have attracted a great deal of attention from both academic and industrial communities.^{4,5} With organoclays,

improvement of the FR property⁵ of polymers can be achieved at relatively low filler loads ($w < 10$ wt %) when compared to the higher filler loads ($w > 40$ %) needed for conventional FR additives, and these nanocomposites can exhibit a higher modulus than neat polymers without sacrificing the toughness.⁵ However, for these nanocomposites, a drastic reduction in flammability would require substantial filler loading exceeding 10 wt %, which may not be economically viable. Very often, even the most efficient organoclays are not sufficiently active to replace conventional FR additives.⁶ The major reason for the insufficient activity of organoclays is their low thermal stability, related to the degradation of organic surfactants in organoclays. Usually, above 170 °C, the organic components in organoclays (e.g., quaternary amine surfactant) start to decompose via the Hoffman elimination process,⁷ releasing combustible alkenes. At the present time, the mechanism of FR activity in organoclays is not completely understood. It has been suggested that the FR mechanism is mostly of a physical nature. Indeed, improved FR properties observed for a variety of polymer–organoclay nanocomposites can be attributed to the presence of nonflammable inorganic particles, higher melt viscosity, reduced gas permeability, and increased char formation, which minimize the flow of burning polymer melt and suppress combustion via reduced fuel feed rates.^{8–10} The combustion residue, formed during the burning of clay-filled nanocomposites, is comprised of multi-

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layered carbonaceous-silicate structures.⁷ The buildup of carbonaceous-silicate chars during burning can result in the retention of fuel and reduced gas permeability. In addition, these layered structures can act as a thermal insulator. The silicate inclusion reinforces the residue, preventing it from breaking apart. In a way, the char enriched by silicate platelets forms a protective barrier to retard the spreading of fire. Thus, we hypothesize that the FR activity of organoclays can be improved by increasing their thermal stability as well as their capability of forming high-temperature residues (i.e., char). The ability to promote charring is particularly desirable for an efficient FR additive.⁹

It has been suggested that the small amount of catalytically active transition metal ions (TMIs) in naturally occurring clays may play a significant role in the charring process of polymer-organoclay nanocomposites. The presence of TMI salts has been shown to improve the FR properties of polymeric materials,¹¹ although the role of TMIs in the polymer combustion and degradation processes has not been fully understood. The poor compatibility between TMI compounds and a polymer matrix is a major concern in the application of TMIs as FR agents for polymers.¹² Thus, we suggest that organoclays, which are more compatible with a broad range of polymers, can serve as a conduit for the introduction of TMIs into polymers. Recently, we demonstrated that the incorporation of catalytically active TMIs into ethylene-vinyl acetate copolymers can generate a new class of nanocomposites with improved FR properties.¹³ The purpose of this study is to understand the relationship between the structure and properties (especially the thermal stability) of organoclays and pristine clays modified with various catalytically active TMIs on the layer surface of each silicate.

In this study, we demonstrated that the use of ion exchange capability in organoclays is an effective means for modifications of organoclays with catalytically active TMI. The modification was also applied to pristine clays, which were used as the reference materials. The resulting TMI-modified organoclays/clays were carefully characterized by atomic absorption spectroscopy (AAS), X-ray absorption near-edge structure (XANES) spectroscopy, elemental analysis (EA), scanning electron microscopy (SEM), simultaneous small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD), thermal gravimetric analysis (TGA), and differential scanning calorimetry (DSC) techniques. Experimental results confirmed that TMIs can be incorporated within the layer silicate stacks, and the content of TMIs in modified clays is close to the limiting value determined by the ion exchange capacity. The improved FR activity of TMI-modified organoclays in the application of nanocomposites has been described earlier.¹³

Experimental

Materials and Preparation. The TMI modification schemes were carried out in two different clay systems: pristine clay (i.e., montmorillonite or Cloisite Na⁺ from Aldrich Chemicals), which was used as a reference material, and a commercially available organoclay (Cloisite C20A from the Southern Clay Company). The C20A organoclay contained the Wyoming Cloisite (also montmorillonite) and dimethyl dihydrogenated tallow quaternary ammonium chloride (DMDTA) surfactant. The content of the surfactant in C20A determined by TGA was 35 wt %. DMDTA is a blend of surfactants prepared from natural products by Akzo Nobel. The major component

Table 1. TMI Salts and Solvents Used in the Modification Procedures

type of clay	solvent used	TMI salt used	concentration [M]
montmorillonite	water	pristine clay	
		copper (II) sulfate	0.3
	methanol	copper (II) chloride	0.3
	ethanol	copper (II) chloride	0.3
	dioxane	copper (II) nitrate	0.3
Cloisite C20A		organoclay	
	methanol	Ni, Cu, Co, and Fe chloride	0.3
	ethanol	copper (II) chloride	0.3
	dioxane	copper (II) nitrate	0.3

in this blend is dimethyl dioctadecylammonium chloride; minor components include (in the order of decreasing content) dimethyl octadecylhexadecylammonium chloride, dimethyl dihexadecylammonium chloride, and a small (<3 wt %) amount of tertiary ammonium chlorides (such as dimethyl octadecylammonium chloride and dimethylhexadecylammonium chloride). All TMI modification processes were carried out in suspensions of pristine clay or organoclay in suitable solvents (Table 1). For example, the organoclay was modified in ethanol, methanol, or dioxane; pristine clay was modified in water at 8 < pH < 10. The choice of solvent was based on two factors: (1) the ability to dissolve TMI compounds, and (2) the ability to penetrate and swell pristine clays/organoclays. Solvents and transition metal salts used in this study were obtained directly from Aldrich Chemicals without further purification. Alcohol used was either methanol or ethanol only.

TMI Modification. Both organoclay and pristine clay samples were thoroughly washed before the TMI treatment. The washing step was necessary to remove excess surfactants in organoclay and impurities in pristine clay. The typical washing procedures were as follows: 2 g of clay sample (organoclay or pristine clay) were placed in 40 mL of solvent (methanol, ethanol, dioxane, or water). The suspension was vigorously stirred for 24 h. Upon stirring for a few hours, the dispersion turned into a viscous slurry due to swelling of the clay. For pristine clay, the slurry was kept in 1 M NaCl solution for 48 h to ensure the removal of exchangeable ion contaminants. The slurry was then filtered and dried in vacuum for 12 h at 80 °C (the weight loss observed for each washed organoclay sample was insignificant).

The washed and dried samples were then placed in appropriate 0.30 M TMI solutions (using the same solvent in the washing process) for ion exchange. The various transition metal salts used, the corresponding solvents and concentrations are summarized in Table 1. The clay suspension was kept in a closed container (to prevent solvent evaporation) under vigorous stirring for 36 h. After the TMI treatment, the samples were filtered, washed again, and dried in a vacuum for 12 h at 80 °C. For TMI-treated organoclays, after the washing step, the recovered solvent was checked for chloride ions using 0.1 N AgNO₃. The washing step was repeated several times until there was no precipitate formation upon the addition of AgNO₃, which ensured the absence of unbound surfactants.

Characterization of TMI Content, Composition, and Oxidation State in Modified Clays. AAS was carried out to determine the amount of TMIs adsorbed by organoclay/pristine clay using a Perkin-Elmer A-Analyst spectrometer. The sample preparation for this analysis was as follows: TMI-modified clays were digested in boiling nitric acid (concentrated) and then heated to dryness. To make sure that TMIs were extracted completely, the extraction step was repeated three times and then the residue was dissolved in deionized water. Solutions were diluted 1:10 before the analysis. The calibration curve was constructed from the absorbance data from reference solutions prepared from standards of known concentrations. Concentrations of TMIs in the tested systems were determined using this calibration curve. In addition, the element analyses for carbon, hydrogen, and nitrogen of TMI-modified pristine clay/organoclay were performed at Schwarzkopf Microanalytical Lab, Inc. (Queens, NY).

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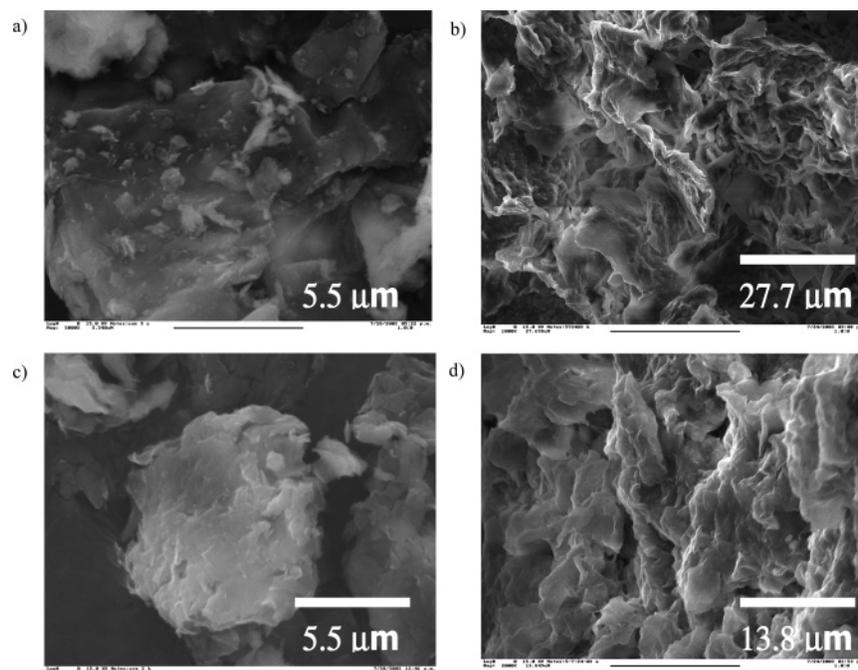


Figure 1. SEM images for the mineral clay montmorillonite and the organoclay Cloisite C20A: (a) montmorillonite as received, (b) montmorillonite modified with copper, (c) C20A as received, and (d) C20A modified with copper.

XANES measurements were carried out to determine the oxidation state of the adsorbed Cu and Fe ions using a PIPS detector at the X18B beamline in the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL). XANES in copper and iron foils were measured in the reference mode and used as energy calibration standards. Reference compounds used in our study were CuO, Cu₂O, FeO(OH), and FeS.

Morphology and Structure Determination. SEM images of clay/organoclay samples before and after modification were taken on a JEOL SEM microscope (JSU-5300). All clay samples were in the form of fine powders and sputter-coated with gold. SEM images were taken using a back-scattering detector. Simultaneous SAXS and WAXD measurements were performed at the X27C beamline in the NSLS, BNL, using two one-dimensional wire detectors, which have been described elsewhere.¹⁴ The chosen X-ray wavelength was 1.366 Å. For SAXS measurement, the sample-to-detector distance was between 800 and 820 mm; for WAXD, the sample-to-detector distance was fixed at 100–130 mm. The scattering angle in SAXS was calibrated using silver bentonite, and the diffraction angle in WAXD was calibrated with aluminum trioxide. All scattering and diffraction profiles were corrected for beam fluctuations and sample absorption.

Thermal Properties. TGA measurements were performed using a TGA-7 analyzer (TA instruments) in a temperature range of 40–800 °C at a heating rate of 20 °C/min. The measurements were carried out in both nitrogen and air environments. DSC measurements were performed using a Mettler Toledo DSC 821 instrument in a temperature range of 0–250 °C. The chosen heating rate was 10 °C/min.

Results and Discussion

In this work, the pristine clay montmorillonite and organoclay C20A were modified using a variety of potentially catalytically active TMI ions, including Cu, Fe, Co, and Ni. The major emphasis was also placed on the investigation of organoclays modified with Cu and Fe salts. The reasons behind the selection of Cu and Fe are as follows:

Table 2. AAS Analysis of the TMI Content in Modified Nanoclays

clay	experimental value [wt %]	expected value ^a [wt %]
organoclay Cloisite C20A	2.6, ^b 2.4, ^c 6.5, ^d 5.5, ^e 4.6, ^f 1.6 ^g	3–4 ⁱ
pristine clay montmorillonite	1.7, ^b 3.5, ^f 1.8, ^g 4.6, ^h	~3 ⁱⁱ

^a The expected value is calculated based on CEC values provided from the following sources: (i) Southern Clay Products; (ii) Ze-Noh Unico (Japan). ^b Copper modifications in methanol as solvent. ^c Iron modifications in methanol as solvent. ^d Cobalt modifications in methanol as solvent. ^e Nickel modifications in methanol as solvent. ^f Copper modifications in dioxane as solvent. ^g Copper modifications in ethanol. ^h Copper modifications in water.

(1) The Cu compounds were extensively studied for use as FR agents and smoke suppressants,¹⁵ so one may expect that the FR activity of Cu-modified organoclays should be good.

(2) The literature data suggest that the FR activity of Cloisite-based organoclays may be at least partially attributed to the presence of iron ions, yet systematic study on this subject is lacking. Thus, we have attempted to explore the relationship between the FR efficiency and the Fe content in organoclays.

Because TMI-modified organoclays are intended to be melt-mixed with polymers, the thermal stability and temperature-resolved structural changes of these materials were thoroughly investigated. The results are summarized as follows:

Characterization of TMIs in Modified Clays. The overall contents of TMIs in organoclay C20A and pristine clay (montmorillonite) were determined by using the AAS technique. Results are listed in Table 2. It is seen that these values strongly depended on the type of solvent used. For example, for organoclay in methanol and pristine clay in water, the amount of TMIs adsorbed was close to the maximum value calculated based on cation exchange capacity (CEC). However, when dioxane was used as the solvent, the Cu contents in both pristine clay and

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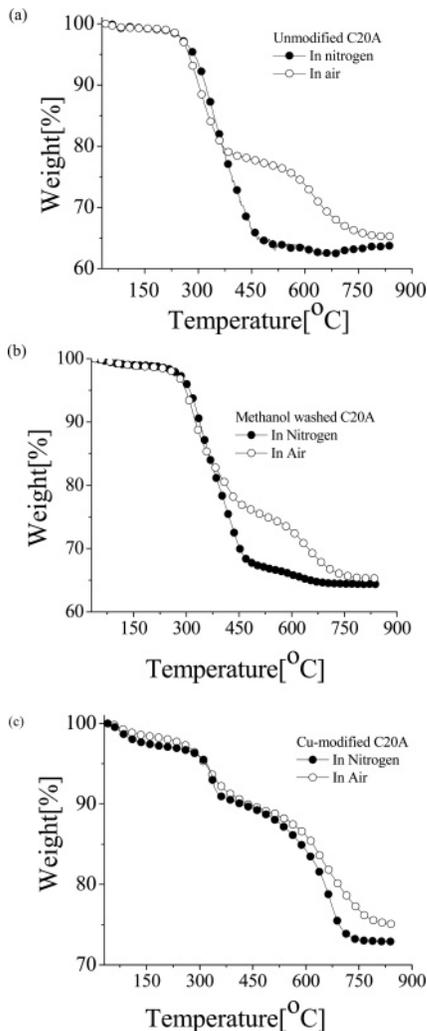


Figure 2. Thermograms of organoclays in different environments: (a) unmodified C20A, (b) methanol-washed C20A, and (c) Cu-modified C20A.

Table 3. EA Results for Unmodified C20A and TMI-Modified C20A

material analyzed	montmorillonite	montmorillonite Cu	C20A	C20A washed	C20A Cu	C20A Fe
carbon	0.36	13.63	28.9	27.23	23.13	25.11
hydrogen	0.74	3.36	6.02	5.53	4.92	5.2
nitrogen	0.01	0.13	0.89	0.84	0.79	0.84
copper	0.00	2.08	0.0	0.0	3.42	0.0
iron	0.90	0.93	1.74	1.56	0.94	4.13
chloride	0.0	0.01	0.01	0.01	3.5	0.1

organoclay exceeded the CEC values, suggesting the possible aggregation of Cu⁺¹ and Cu⁺² ions and/or the formation of colloid particles in the interlayer space. It should be pointed out that, in the case of organoclay, the overall amount of absorbed Cu ions combined with the residual surfactant seemed to exceed the overall ion exchange capacity. These unexpected results were obtained by the EA, which will be discussed next. We suggest that the excessive TMI content is due to the adsorption of TMI, not in the form of individual ions but as multinuclei complexes or colloid particles. This possibility is discussed in greater detail below.

The results from the element analysis of unmodified organoclay, pristine clay, and TMI-modified nanoclays are listed in Table 3. It is seen that even as received from the manufacturer, pristine clay (montmorillonite) contained a significant amount of iron. Since montmorillonite was pretreated by the manufacturer

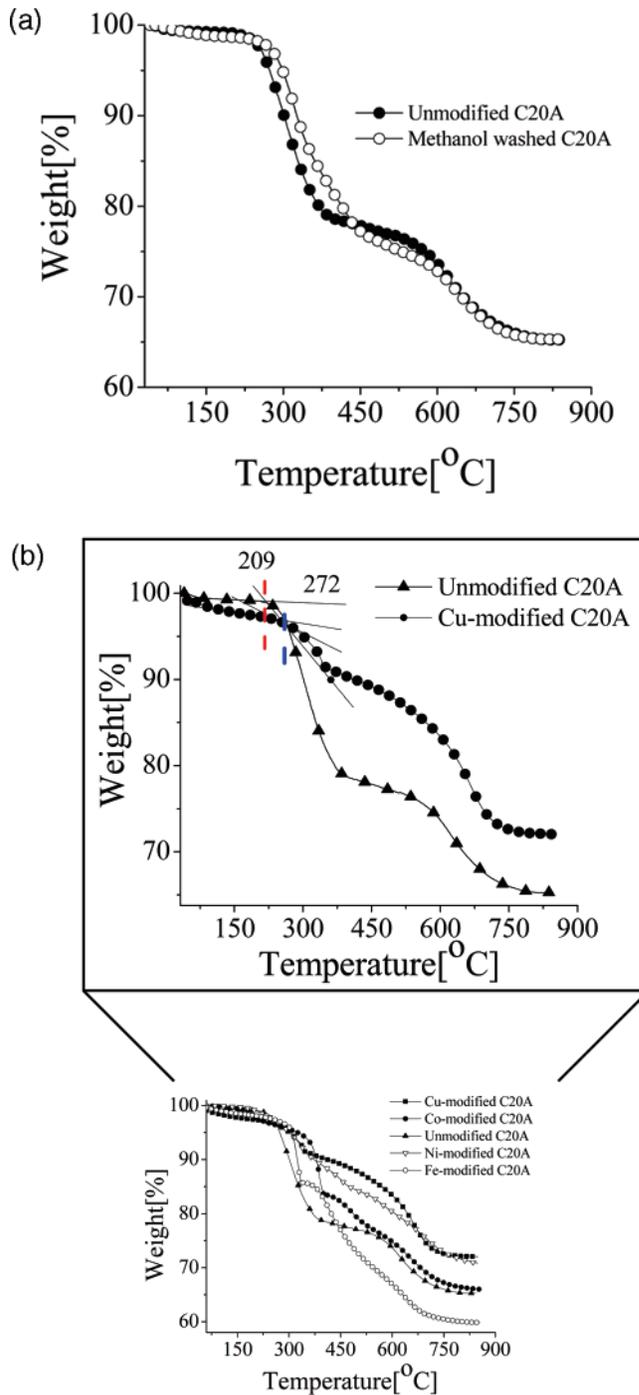


Figure 3. Thermograms of organoclays in air: (a) unmodified C20A vs methanol-washed C20A and (b) unmodified C20A vs TMI-modified C20A.

to remove exchangeable ion contaminants, we suggest that the iron detected in pristine clay (montmorillonite) probably exists within the crystalline lattice of the clay layers, thus it can be termed as structural iron. On the other hand, the Fe content in the as-received organoclay (C20A) from the Southern Clay was higher than that of pristine clay. This unexpected result suggests that some additional iron atoms were trapped within the Cloisite mineral during the modification process by organic surfactant. Because the content of chlorine in unmodified C20A was negligibly low, excessive iron might be present in the form of iron oxide or hydroxide deposited between the clay layers. It is seen that the modification by FeCl₃ in methanol greatly increased the Fe content in C20A. However, in FeCl₃-modified C20A, the

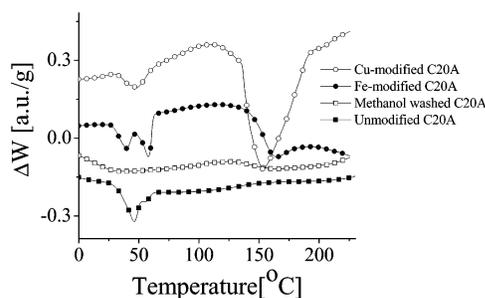


Figure 4. DSC curves for unmodified C20A compared with TMI-modified C20A.

Table 4. Estimation of Char Content Based on Results from TGA and EA

material analyzed	C20A	C20A washed	C20A Cu	C20A Fe
carbon	28.9	27.23	23.13	25.11
hydrogen	6.02	5.53	4.92	5.2
nitrogen	0.89	0.84	0.79	0.84
degradable CHN %	35.81	33.6	28.84	31.15
weight loss TGA	34.5	34.5	27.0	40.0
corrected weight loss for residual water	30.82	30.82	23.32	36.32
corrected weight loss for solvent	29.82	29.32	20.32	34.87
amount of char estimated at 800 °C in air	5.99	4.28	8.52	3.67

Table 5. DSC Results for Unmodified C20A and TMI-Modified Organoclays

sample	ΔH [J/g]	ΔH_1 [J/g]
C20A as-received	20.00	
C20A washed with methanol	14.00	
C20A modified with Cu^{2+}	8.50	116.0
C20A modified with Ni^{2+}	3.00	80.00
C20A modified with Co^{2+}	3.00	98.70
C20A modified with Fe^{3+}	7.00	120.00

content of chlorine was very low, and the overall surfactant content (calculated from combined C, H, and N concentrations) was only slightly reduced compared to that of unmodified C20A. Thus, it is likely that Fe in organoclay is precipitated in the form of iron oxide. Furthermore, the C:N molar ratios in modified and unmodified C20A systems are very similar and correspond to the value calculated for DMDHTA surfactant. This confirms that DMDHTA is the major organic component in modified organoclays, while the contribution of trapped methanol is insignificant. By considering the Fe present in montmorillonite mineral as a structural component (i.e., included into a mineral lattice), we can evaluate the content of nonstructural iron in C20A (i.e., it is presumably located in the interlayer space).

The overall content of Cu ions in Cu-modified C20A combined with the residual surfactant content also exceeds the value calculated based on the overall CEC in organoclay. In contrast to the Fe-modified system, CuCl_2 -modified organoclay contained a significant amount of chlorine. The Cu/Cl molar ratio in Cu-modified organoclay was 1:1.9, suggesting the partial reduction of Cu^{2+} , which might occur due to the presence of primary amines or unsaturated surfactants or residual solvent (methanol) acting as a reducing agent. Although the decreases in C, H, and N components in TMI-modified organoclays indicate that the exchange might have taken place, it is conceivable that instead of a complete exchange of surfactant cations in organoclay, partially reduced CuCl_2 may form molecular complexes with them, where CuCl_2 and CuCl molecules are trapped between the mineral layers. We note that all modified compounds were

thoroughly washed during the modification process, so that the deposition of CuCl_2 crystallites on the surface of clay particles is unlikely. In addition, the alcohol-washing step should also remove unbound surfactants. It is interesting to note that the treatment by CuCl_2 results in reduction of the nonstructural iron content in the organoclays. The oxidation states of Cu and Fe deposited within the organoclay stacks were investigated using XANES, SEM, and X-ray scattering; their results are discussed next.

Structure, Morphology, and Thermal Stability of TMI-Modified Clays. Organoclays and pristine clays containing TMIs (e.g., modified by CuCl_2 or FeCl_3), if precipitated from organic solvent or water, could form distinct crystallites, which would appear in SEM micrographs as bright spots. Their shape would depend on the crystal structure of TMI. In this study, the SEM micrographs did not show any deposition of TMI salts on the surface of unmodified or TMI-modified clays (Figure 1). The absence of crystalline salt deposits on the surface of clay stacks in spite of the significant overall content of Fe and Cu in all tested materials suggests that TMIs are probably deposited between the silicate layers.

For all tested organoclays, TGA results showed that the corresponding weight loss was found to be more pronounced in nitrogen than in air (Figure 2), which could be attributed to the charring process, that is, the formation of thermally stable mineralized char. As evident by the EA results, the washing step by cold methanol did not cause a significant decrease in the overall surfactant content in C20A. However, the treatment significantly shifted the onset temperature of thermal degradation toward a higher value, thus increasing the thermal stability of organoclay in air (Figure 3a). We hypothesize that the effect of methanol washing is due to the removal of thermally unstable, polar primary and secondary amine contaminants present in DHDHTA surfactant, thus resulting in the enhanced thermal stability of the surfactant component in the organoclays.

By comparing the results of element analysis and TGA data (Figure 3b and Table 4), the weight loss at 850 °C in all tested samples was found to be below the expected value based on the combined carbon, hydrogen, and nitrogen (C, H, and N) content determined from the element analysis. In pure surfactant DHDHTA, which is the only source of C, H, and N in organoclays, the compound should completely degrade below 800 °C without leaving solid residue. Thus, in the absence of charring and thermal degradation of the clay mineral, the overall weight loss should correspond to the combined content of C, H, and N elements. (We note that montmorillonite mineral undergoes structural dehydroxylation above 600 °C, losing water in the octahedral layers.¹¹) In C20A, the weight loss can be attributed to several processes: (1) loss of residual solvent due to evaporation below 80 °C, (2) degradation of organic surfactants above 250 °C, and (3) dehydroxylation of the mineral phase above 600 °C (the mineral fraction of C20A is about 65%). Thus, the contribution due to the dehydroxylation proceeds within the overall weight loss in C20A (ΔW_{str} = change in weight due to loss of water) must be accounted for. Assuming that the presence of surfactant in organoclays does not affect the dehydroxylation process, we suggest that ΔW_{str} may be evaluated as follows:

$$\Delta W_{\text{str}} = \Delta W_{\text{MNa}} \cdot x \quad (1)$$

where ΔW_{MNa} is the weight loss due to dehydroxylation in pristine clay (montmorillonite) within the temperature range of 600–800 °C, determined by TGA, and x represents the content of the mineral in the organoclay (i.e., 65% in C20A).

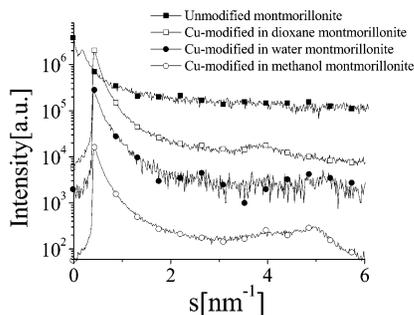


Figure 5. SAXS traces for montmorillonite mineral clay modified using TMI solutions in different solvents, showing the effect of solvent on the d -spacing.

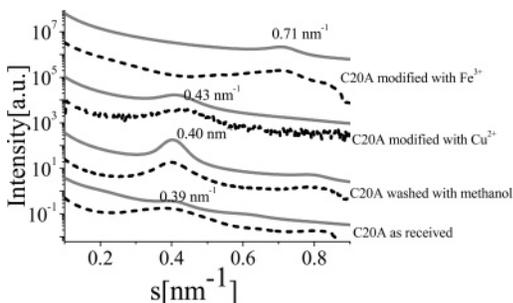


Figure 6. SAXS profile of C20A organoclay modified with various TMIs (Cu^{2+} and Fe^{3+}) compared with that of unmodified C20A and methanol-washed C20A (solid line represents the calculated value, and dashed line represents the experimental data).

The maximum expected weight loss (ΔW_{\max}), resulting from the complete degradation of the surfactant component and the dehydroxylation process, can be evaluated as follows:

$$\Delta W_{\max} = W_C + W_H + W_N + \Delta W_{\text{str}} \quad (2)$$

where W_C , W_H and W_N are the contents of C, H, and N [wt %], respectively, determined from the element analysis. In the above equation, we assumed that the char content, W_{char} , can be evaluated as the difference between ΔW_{\max} and the experimental weight loss ΔW_{TGA} :

$$W_{\text{char}} = \Delta W_{\max} - \Delta W_{\text{TGA}} \quad (3)$$

From TGA results, it is interesting to see that the introduction of ~ 3.5 wt % of Cu resulted in an increase of the onset degradation temperature by almost 63 $^{\circ}\text{C}$, drastically enhancing the thermal stability of TMI-modified organoclays. Also, the introduction of Cu into the organoclay significantly increased the char content compared to that of the as-received unmodified and methanol-washed organoclays. It should be noted that, for Cu-modified clays, CuCl_2 can either remain stable during heating in dry air to 800 $^{\circ}\text{C}$ or transform into copper oxide (CuO). Thus, the thermal degradation process should either remain constant or decrease by 2% of the total organoclay weight. Because we tried to make a conservative estimate of the char content, we did not account for the degradation of CuCl_2 . If we account for the oxidation process of CuCl_2 , it would result in a higher estimate for W_{char} .

The shape of TGA curve for Fe-modified organoclays showed that the modification by Fe shifted the onset degradation temperature toward a higher value compared to that of the unmodified organoclays. However, the extent of shift was less than that in Cu-modified organoclays. In contrast to Cu-modified organoclays, the introduction of Fe into organoclays resulted in reduced char formation, that is, the experimental weight loss approached ΔW_{\max} . This indicates that the Fe-modified orga-

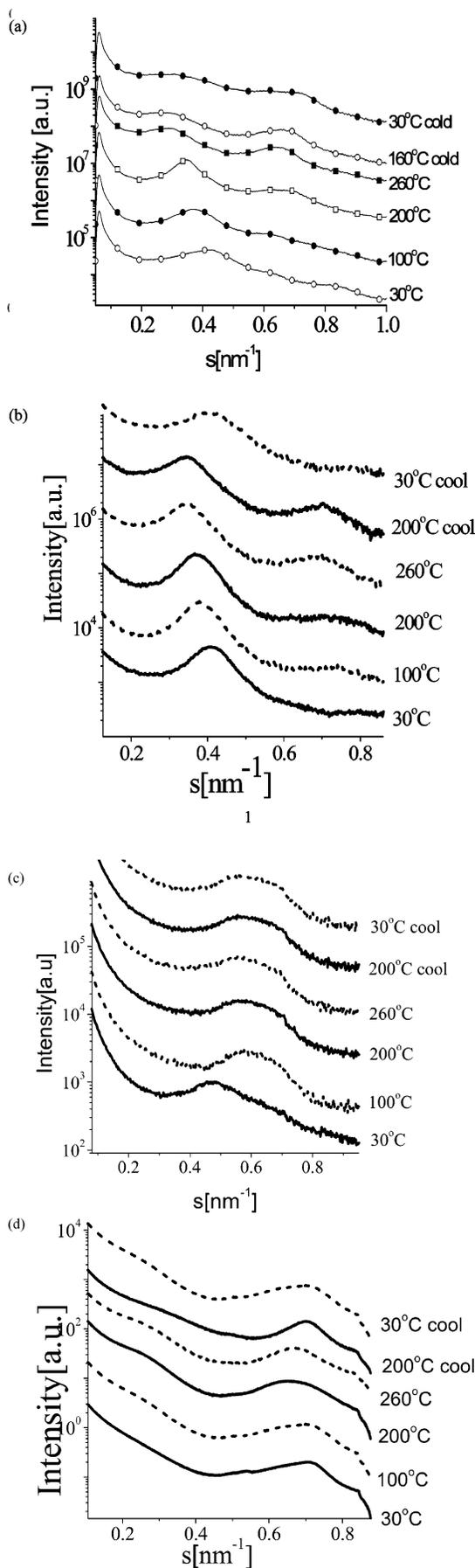


Figure 7. Temperature-resolved SAXS profiles for (a) unmodified C20A, (b) methanol-washed C20A, (c) Cu-modified C20A, and (d) Fe-modified C20A.

Table 6. Parameters of Layer Thickness Distribution for C20A Organoclay and Its TMI-Modified Derivatives as Determined from SAXS Data

	C20A as received	C20A washed with methanol	C20A modified with copper (Cu ²⁺)	C20A modified with iron (Fe ³⁺)
average number of layers (N)	5	6	6	20
average long period first mode r_1 (nm)	2.4	2.45	2.33	1.30
standard deviation long period first mode σ_1 (nm)	1.70	0.55	1.0	0.3
average long period second mode r_2 (nm)	4.80	3.00		1.60
standard deviation long period second mode σ_2 (nm)	0.50	0.30		0.30
fraction of major organic mode f_1	0.75	1.00	1.00	0.70
fraction of minor organic mode f_2	0.25	0	0	0.30

noclays have a lower efficiency of char formation or that iron oxide can catalyze the combustion of char at lower temperatures, where the char becomes volatile at temperatures approaching 800 °C.

On the basis of the above TGA results, it is clear that the modification by TMIs distinctly shifted the onset degradation temperature of modified organoclays toward higher values compared to that of unmodified organoclays, although the degree of onset temperature changed with various TMIs (Figure 3b). In addition, the charring process became enhanced when the organoclays were modified by various TMIs, such as Cu, Fe, Ni, and Co, as evidenced from the TGA curve. It is interesting to note that Ni and Cu showed almost an equivalent amount of residue at around 800 °C.

In our previous work,¹⁶ we showed that the surfactant component in C20A organoclay could undergo a melt-like transition (T_{tr1}) in the temperature range of 30–50 °C, which is about 20 °C below the melting temperature of pure DMDHTA surfactant. The solvent treatment did not cause a significant shift in the transition temperature, but resulted in a drastic decrease in the enthalpy change, ΔH of the organoclays listed in Table 5. In Figure 4, a large endothermic transition in the vicinity of $T_{tr2} = 150$ °C was also detected in TMI-modified organoclays. Although the exact nature of this high-temperature transition is not well understood, we hypothesize that it is related to the dissociation of the TMI–surfactant complex. This is because the high-temperature transition is only in the presence of TMIs, where the corresponding ΔH is rather high but the weight loss is insignificant in the vicinity of 150 °C, as determined by TGA. As a result, the observed transition cannot be attributed to the loss of solvent or surfactant due to evaporation or thermal degradation. In addition, the melting temperature of DMDHTA surfactant is significantly lower than T_{tr2} , so it is unlikely that the surfactant melting can induce such intense endothermic peaks.

Structural Changes at Elevated Temperatures. The TMI modification resulted in drastic changes in the SAXS profiles for both pristine clay (Figure 5) and organoclay systems (Figure 6). It is thought that the penetration of TMIs in the interlayer spacing of clay stacks (i.e., the gallery spacing) would most likely decrease the d -spacing value. This is generally consistent with the SAXS observations. In all TMI-modified pristine clays, the average d -spacing was found to decrease, manifesting itself by shifting the SAXS maxima toward higher s values ($s = 2\lambda^{-1} \sin \theta$, where 2θ is the scattering angle and λ is the wavelength). The magnitude of the shift strongly depended on the solvent type (Figure 5). In contrast to solvents such as water, methanol, and ethanol, the pristine clay modified by TMIs in dioxane exhibited an increase in d -spacing. This may be due to the colloidal formation or aggregation of ions. Furthermore, there is the possibility of complex formation with surfactants in organoclays. These results

were used as the reference information for the comparison of TMI-modified organoclays.

In as-received C20A organoclay, the scattering peaks are nonequidistant at the s scale, indicating the existence of dual thickness distributions of organomineral layers, where some layers overloaded with surfactant above the average CEC coexist with layers of lower surfactant content in the same stacks.¹⁶ As evidenced from the EA and TGA data, the washing treatment using methanol did not cause any significant change in the overall surfactant content. However, it drastically changed the shape of the SAXS profiles (Figure 7). It was seen that after washing by alcohol, the scattering peaks shifted toward equidistant positions at the s scale. This suggests the formation of a more uniform layer thickness distribution compared to the original C20A organoclay. In other words, redistribution of the surfactant component took place within the clay structure. Modification by CuCl₂, as well as by FeCl₃, resulted in an abrupt shift in the scattering maxima toward higher s values, indicating that the treatment by TMIs resulted in a decrease in d -spacing.

In agreement to the TGA results, temperature-resolved SAXS profiles showed that the as-received C20A organoclay underwent rapid degradation above 200 °C, which manifested itself by the broadening and shifting of the scattering peaks (Figure 7a) that has been observed before.¹⁶ On the other hand, the SAXS peaks retained their shape in methanol alcohol-washed materials up to 260 °C, confirming the increase in thermal stability¹⁷ (Figure 7b) that can be attributed to a loss of loosely held surfactants as well as organic contaminants from surfactants. The TMI modification resulted in radical changes in the character of the temperature dependence of the SAXS pattern. In both Fe-modified and Cu-modified organoclays, the scattering maxima shifted to higher s values compared to those of unmodified C20A, indicating a decrease in d -spacing in the temperature range of 30–280 °C (Figure 7c,d). It is interesting to note that the temperature-resolved SAXS profiles for Cu- and Fe-modified organoclays showed a minimal change in the shape or location of the scattering maxima throughout the whole range of tested temperatures, which is consistent with higher thermal stability as observed by TGA. These observations verified that TMIs penetrated into the interlayer space in organoclay and probably formed a complex with the surfactant layer surface. We hypothesize that the TMI deposits may form a “pillar-like” structure in the interlayer gallery, such that the organic layer thickness no longer depends on the conformation of surfactant molecules but is determined by the thermal stability of TMI aggregates located between clay layers.

It was seen that the SAXS maxima in TMI-modified organoclays were broadened and shifted toward higher s values. These SAXS profiles were modeled using a method previously developed by us.¹⁶ The parameters used for given calculations

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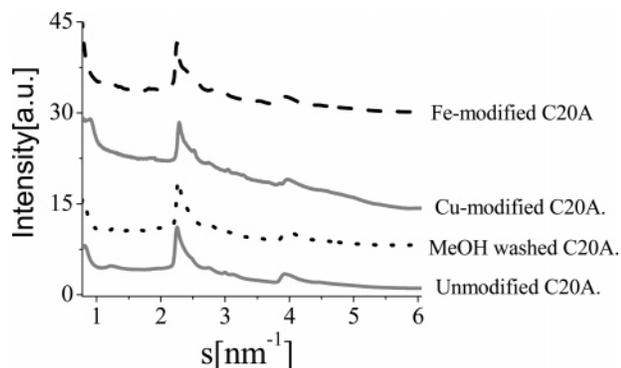


Figure 8. WAXD profile of unmodified C20A, methanol-washed C20A, and TMI (Cu^{2+} and Fe^{3+})-modified C20A.

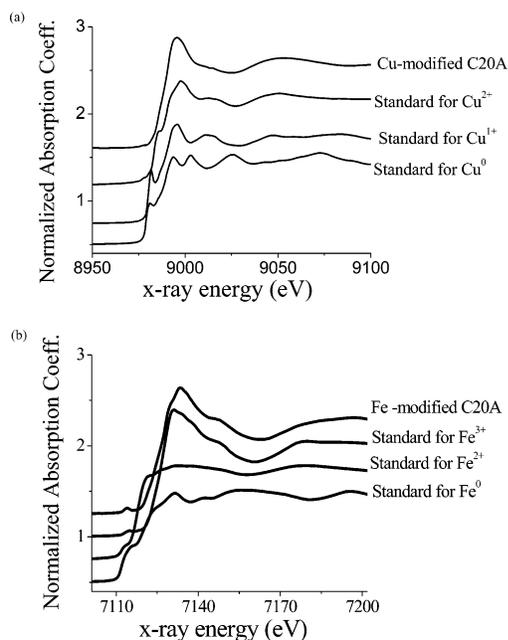


Figure 9. Extended X-ray absorption fine structure profiles for organoclay C20A and its TMI derivatives: (a) Cu-modified C20A and (b) Fe-modified C20A.

in organoclays before and after the TMI treatment are given in Table 6. The calculated and experimental results are compared in Figure 6, where the modeling effort appears to yield some meaningful parameters. The comparison results indicate that a rather broad layer thickness distribution in TMI-modified organoclay systems existed. It is interesting to note that the DSC transition observed in the vicinity of 150 °C did not correspond to detectable changes in SAXS profiles for both Fe-modified and Cu-modified organoclays. This is consistent with the proposed pillar-like structure within the interlayer space of clays by TMI aggregates. Broadening of SAXS peaks can be attributed to the formation of different types of TMI–surfactant–organoclay complexes with different average TMI loads and, hence, different average d -spacings. These observations are consistent with the structural heterogeneity of Cloisite clays previously described.¹⁶

TMI modification did not exhibit a detectable effect on the WAXD profiles of organoclays at room temperature (Figure 8). It is imperative to note that crystal reflection peaks corresponding to CuCl_2 , FeCl_3 crystals, or iron oxide deposits were not observed in WAXD profiles, suggesting the absence of deposits of TMI salts on the clay surfaces. This is in agreement to the SEM data where no crystallites of TMIs were observed on the surface of clays. Thus, the shift of SAXS peaks indicates that TMIs intercalate in the gallery spacing of organoclays.

Oxidation State of TMIs in Modified Organoclays. In this section, we focus mainly on the ion exchange of TMIs in the interlayer spacing of clays. Cu- and Fe-modified C20A organoclays were investigated by XANES. The standard compounds of Cu^0 , Cu^{1+} , and Cu^{2+} , as well as Fe^0 , Fe^{2+} , and Fe^{3+} were used as the references to determine the oxidation state of Cu and Fe, respectively, in organoclays. The Cu K-edge for organoclays modified with copper was found near the Cu^{1+} edge position (Figure 9). This suggests that, in the Cu-modified organoclays, copper ion is not in the +2 oxidation state, but it is in the oxidation state of +1. Thus, this finding indicates that a partial reduction from Cu^{2+} to Cu^{1+} has taken place, which is reasonable because of the presence of primary amines and unsaturated surfactants. This is also consistent with our earlier argument about the partial reduction of CuCl_2 based on results from the EA (Table 3). In the case of Fe-modified C20A, its oxidation state remained stable, as the edge of the modified clay was very similar to that of Fe^{3+} . This finding is also consistent with the EA results in Table 3. We hypothesize that iron was deposited in the oxide form within the interlayer gallery.

Conclusions

Organoclays modified by TMIs were investigated using structural techniques (SEM, SAXS, WAXD, and XANES), thermal analysis (TGA and DSC) and chemical composition analysis (AAS and EA) techniques. It seems that some loosely bound exchangeable surfactant ions in organoclays can facilitate TMI penetration into the interlayer galleries and result in the loss of surfactant evidenced by AAS and EA examinations. All tested TMIs (e.g., Cu and Fe) were found to predominantly deposit in the interlayer space, which is constant with the SEM, SAXS, and WAXD results. In Cu-modified organoclays, the oxidation state of Cu as determined by XANES was that of Cu^{1+} . In Fe-modified organoclays, Fe was predominantly present in the Fe^{3+} oxidation state. TMIs may form aggregates within the organic layer, resulting in a pillar-like structure and decreased d -spacing, but enhanced thermal stability. SAXS results indicated that the layer structure of TMI-modified organoclays persisted at temperatures as high as 260 °C, above the degradation temperature of conventional organoclays. As indicated by TGA, the onset temperature of the thermally induced weight loss in TMI-modified organoclays was shifted toward a higher value, and the amount of final char formed after thermal degradation was higher than that formed in unmodified organoclays. The higher thermal stability of TMI-modified organoclays can be attributed to the charring processes, facilitated by the presence of catalytically active TMIs. In addition, the TGA data showed that, while washing organoclays by methanol may slightly increase the thermal properties of organoclays and this can be accounted for by the loss of loosely held surfactant and organic contaminants, drastic enhancement of thermal stability is accomplished by the introduction of TMIs in the organoclays. The high thermal stability of TMI-modified organoclays may be used as more effective FR agents.

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